Claims

1. A method of producing an alumina-supported catalyst, which comprises the following steps: a first impregnation step in which an initial alumina support material is impregnated with a source of a 2-valent metal capable of forming a spinel compound with alumina;

a first calcination step in which the impregnated alumina support material is calcined at a temperature of at least 550°C to produce a modified alumina support material;

a second impregnation step in which the modified alumina support material is impregnated with a source of catalytically active metal;

and a second calcination step in which the impregnated modified support material is calcined at a temperature of at least 150°C.

2. A method as claimed in Claim 1, in which the initial alumina support material at least predominantly comprises γ-alumina.

3. A method as claimed in Claim 1 or Claim 2, in which the impregnated modified support material is calcined at a temperature of up to 600°C.

4. A method as claimed in any preceeding claim, in which the impregnated and calcined modified support has a pore volume measured by nitrogen BET in which at least half the pore volume is constituted by pores larger than 30 nm in diameter.

5. A method as claimed in any preceding Claim, in which the initial alumina support material has a specific surface area in the range 100 to 300 m^2/g.

6. A method as claimed in any preceding Claim, in which the initial

alumina support material comprises essentially spherical particles having a particle size range whereby at least 80 volume % fall in the range 25 to 150 μm.

7. A method as claimed in any preceding Claim, in which the initial alumina support material has a pore volume greater than $0.2cm^3/g$, preferably greater than $0.4cm^3/g$.

8. A method as claimed in any preceding Claim, in which the first calcination step is carried out at a temperature in the range 800 to 1200°C.

9. A method as claimed in any preceding Claim, in which the first calcination step is carried out at a temperature in the range 900 to 1200°C.

10. A method as claimed in any preceding Claim, in which the modified alumina support has a surface area of less than 40 m2/g.

11. A method as claimed in any preceding Claim, in which the modified alumina support has an ASTM attrition value of less than 20 % by weight of fines produced by 5 hours testing

12. A method as claimed in any preceding Claim, in which the modified alumina support has an ASTM attrition value of less than 8 % by weight of fines produced by 5 hours testing

13. A method as claimed in any preceding Claim, in which the modified alumina support comprises at least 10 % by weight of alfa-alumina.

14. A method as claimed in any preceding Claim, in which the source of a

2-valent metal comprises a source of cobalt, zinc, magnesium, manganese, nickel or iron.

15. A method as claimed in any preceding Claim, in which the source of a 2-valent metal does not comprise a source of cobalt.

16. A method as claimed in any preceding Claim, in which the source of a 2-valent metal comprises nickel.

17. A method as claimed in any preceding Claim, in which the source of a 2-valent metal comprises nickel in an amount of less than 20 wt% of the final reduced catalyst.

18. A method as claimed in any preceding Claim, in which the source of a 2-valent metal comprises nickel in an amount of less than 8 wt% of the final reduced catalyst.

19. A method as claimed in any preceding Claim, which includes additionally impregnating or co-impregnating the alumina support material with a promoter.

20. A method as claimed in Claim 19, in which the promoter comprises platinum or rhenium.

21. A method as claimed in Claim 20, in which the promoter is rhenium and the source of rhenium is selected from perrhenic acid ($HReO_4$), ammonium perrhenate, rhenium halide(s) and rhenium carbonyl(s).

22. A method as claimed in any preceding Claim, which includes

additionally incorporating a stabiliser into the alumina support material with a stabiliser.

23. A method as claimed in Claim 22, in which the stabiliser comprises lanthanum.

24. A method as claimed in any preceding Claim, in which the first impregnation step comprises an incipient wetness treatment in which an aqueous solution of the 2-valent metal compound is mixed with the dry support material until the pores are filled, and the impregnated support is then dried, prior to the first calcining step.

25. A method as claimed in any preceding Claim, in which the source of catalytically active metal comprises a source of cobalt.

26. A method as claimed in Claim 25, in which the source of cobalt is selected from cobalt nitrate ($Co(NO_3)_2$), cobalt acetate(s), cobalt halide(s), cobalt carbonyl(s), cobalt oxalate(s), cobalt phosphate(s), cobalt carbonate(s), cobalt (hexa)amine salt(s) and organic cobalt compounds.

27. A method as claimed in Claim 25 or Claim 26, in which the second impregnation step comprises an incipient wetness treatment in which an aqueous solution of a cobalt compound and optionally a rhenium compound is mixed with the modified support material until the pores are filled and the impregnated modified support material is then dried, prior to the second calcination step.

28. A method as claimed in Claim 24 or Claim 26 or Claim 27, in which the amount of aqueous solution used in the impregnation is 0.05-2 times larger

than the measured pore volume of the catalyst support.

29. A method as claimed in Claim 24 or any of Claims 26 to 28, in which drying is carried out at 80 to 120°C.

30. A method as claimed in any preceding Claim, in which, after the second calcination step, the alumina-supported catalyst material is activated.

31. A method as claimed in Claim 30, in which the activation step comprises reduction of a substantial portion of the catalytically active metal compound present to the metal.

32. A method as claimed in Claim 31, in which the reduction is carried out by treating the catalyst material with a reducing gas.

33. A method as claimed in Claim 32, in which the reducing agent is hydrogen and/or carbon monoxide, optionally mixed with an inert gas.

34. A method as claimed in any of Claims 31 to 33, in which the reduction is carried out at an activation temperature of 250 to 500°C.

35. A method as claimed in Claim 34, in which the activation temperature is in the range 300 to 450°C.

36. A method as claimed in any preceding Claim, in which, prior to impregnation, the alumina support has an ASTM attrition value of less than 30% by weight of fines produced by 5 hours testing.

37. A method as claimed in Claim 36 in which the ASTM value is less than

20%.

38. A catalyst material produced by a method as claimed in any preceding Claim.

39. A catalyst as claimed in Claim 38, in which the catalytically active metal and optionally the 2-valent metal are cobalt, and the cobalt content of the catalyst is from 10 to 40% by weight.

40. A catalyst as claimed in Claim 39, in which the cobalt content is from 15 to 25% by weight.

41. A catalyst as claimed in any of Claims 38 to 40, incorporating less than 3% by weight of a promoter.

42. A catalyst as claimed in Claim 41, in which the promoter is rhenium or platinum.

43. A catalyst as claimed in any of Claims 38 to 42, in which the initial support material predominantly comprises γ-alumina .

44. A catalyst as claimed in Claim 43, in which the γ-alumina is stabilised with a stabilising agent, optionally lanthanum.

45. A catalyst as claimed in any of Claims 38 to 44, in which the alumina support material includes a binder.

46. A catalyst as claimed in Claim 45, in which the binder represents less

than 25% by weight of the catalyst.

47. A catalyst as claimed in Claim 45 or Claim 46, in which the binder is an alumina-containing binder material.

48. A catalyst as claimed in any of Claims 38 to 47, in which the specific surface area of the prepared catalyst, comprising the cobalt on the modified support, is up to 150 m^2/g.

49. A catalyst as claimed in any of Claims 37 to 48, in which the pore volume of the prepared catalyst is from 0.05 to 0.7 cm^3/g.

50. A catalyst as claimed in any of Claims 37 to 49, in which the pore diameter of the prepared catalyst is at least 10 nm, preferably at least 18 nm.

51. The use of a catalyst as claimed in any of Claims 48 to 50 in a Fischer-Tropsch synthesis reaction.

52. A use as claimed in Claim 51, in which the reaction is carried out in a slurry bubble column reactor.

53. A use as claimed in Claim 52, in which H_2 and CO are supplied to a slurry in the reactor, the slurry comprising the catalyst in suspension in a liquid including the reaction products of the H_2 and CO, the catalyst being maintained in suspension in the slurry at least partly by the motion of the gas supplied to the slurry.

54. A process for the production of hydrocarbons which comprise subjecting H_2 and CO gases to a Fischer-Tropsch synthesis reaction in a reactor in the

presence of a catalyst as claimed in any of Claims 28 to 40.

55. A process as claimed in Claim 54, in which the reaction is a three-phase reaction in which the reactants are gaseous, the product is at least partially liquid and the catalyst is solid.

56. A process as claimed in Claim 55, in which the reaction is carried out in a slurry bubble column reactor.

57. A process as claimed in Claim 56, in which the H_2 and CO are supplied to a slurry in the reactor, the slurry comprising the catalyst in suspension in a liquid including the reaction products of the H_2 and CO, the catalyst being maintained in suspension in the slurry at least partly by the motion of the gas supplied to the slurry.

58. A process as claimed in any of Claims 54 to 57, in which the reaction temperature is in the range 190-250°C.

59. A process as claimed in Claim 58, in which the reaction temperature is in the range 200-230°C.

60. A process as claimed in any of Claims 54 to 59, in which the reaction pressure is in the range 10-60 bar.

61. A process as claimed in Claim 60, in which the reaction pressure is in the range 15 to 30 bar.

62. A process as claimed in any of Claims 54 to 61, in which the H_2/CO ratio of the gases supplied to the Fischer-Tropsch synthesis reactor is in the

range 1.1 to 2.2.

63. A process as claimed in Claim 62, in which the H_2/CO ratio is in the range 1.5 to 1.95.

64. A process as claimed in any of Claims 54 to 63, in which the superficial gas velocity in the reactor is in the range 5 to 60 cm/s.

65. A process as claimed in Claim 64 in which the superficial gas velocity is in the range 20 to 40 cm/s.

66. A process as claimed in any of Claims 54 to 65, in which the product of the Fischer-Tropsch synthesis reaction is subsequently subjected to post-processing.

67. A process as claimed in Claim 66 in which the post-processing is selected from de-waxing, hydro-isomerisation, hydro-cracking and combinations of these.

68. A method for the production of an alumina support for a catalyst, which comprises impregnating an initial alumina support material with a source of a 2-valent metal capable of forming a spinel compound with alumina, and calcining the impregnated alumina at a temperature of at least 550°C.

69. A method as claimed in Claim 68, in which the initial alumina support material at least predominantly comprises γ-alumina.

70. A method as claimed in Claim 68 or Claim 69, in which the initial alumina support material has a specific surface area in the range 100 to 300

m^2/g.

71. A method as claimed in any of Claims 68 to 70, in which the initial alumina support material comprises agglomerated essentially spherical particles having a particle size range whereby at least 80% fall in the range 30 to 120 μm.

72. A method as claimed in any of Claims 68 to 71, in which the initial alumina support material has a pore volume greater than $0.2cm^3/g$, preferably greater than $0.4cm^3/g$.

73. A method as claimed in any of Claims 68 to 72, in which the impregnated alumina support material is calcined at a temperature in the range 800 to 1200°C.

74. A method as claimed in any of Claims 68 to 73, in which the source of a 2-valent metal comprises a source of cobalt, zinc or magnesium.

75. A method as claimed in any of Claims 68 to 74, which includes additionally impregnating the alumina support material with a promoter.

76. A method as claimed in Claim 75, in which in which the promoter comprises platinum or rhenium.

77. A method as claimed in Claim 76, in which the promoter is rhenium and the source of rhenium is selected from perrhenic acid ($HReO_4$), ammonium perrhenate, rhenium halide(s) and rhenium carbonyl(s).

78. A method as claimed in Claim 77, in which the source of the 2-valent

metal compound is cobalt nitrate and the rhenium compound is perrhenic acid.

79. A method as claimed in Claim 68 to 78, which includes additionally impregnating the alumina support material with a stabiliser.

80. A method as claimed in Claim 79, in which the stabiliser comprises lanthanum.

81. A method as claimed in any one of Claims 68 to 80, in which the first impregnation step comprises an incipient wetness treatment in which an aqueous solution of the 2-valent metal compound and optionally a rhenium compound is mixed with the dry support material until the pores are filled, and the impregnated support is then dried, prior to the second calcining step.

82. A method as claimed in any of Claims 68 to 81, in which the amount of aqueous solution used in the impregnation is 0.05-2 times larger than the measured pore volume of the catalyst support.

83. A method as claimed in any of Claims 81 to 82, in which the drying is carried out at 80 to 120°C.